Final Report

March 21st, 1996

ONR Contract N00014-95-1-0797

Title: Molecular Tribology

Amount: $5,600

Period: 1 April 1995 to 30 March 1996

Contract Monitor: Peter Schmidt

Principal Investigator: Mathew Mate

This contract provided funding for a Symposium entitled "Molecular Tribology" which was part of the American Chemical Society National Meeting held in Anaheim, California, April 4-6, 1995. Attendees, about 40 per session, came from many diverse disciplines - chemistry, physics, engineering, etc. - but all had a common interest in the molecular origins of tribology. Thirty four papers were presented on the following topics:

(i) atomic-scale simulations of tribology phenomena;

(ii) UHV surface science, atomic force microscopy, and surface force apparatus studies of the molecular origins of tribology;

(iii) tribological issues faced by the space, automotive, magnetic recording, and micro-mechanics industries.

Funding from the ONR grant was used to provide partial travel support for four of the twelve invited speakers. The program and abstracts are attached.

Symposium on Molecular Tribology

Division of Colloid Chemistry and Surface Chemistry

American Chemical Society National Meeting

Tuesday Morning, April 4, 1995

Park Ballroom C

Chair: J. Krim

9:00 - Introductory Remarks

9:05 - Interfacial Junctions, Confined Molecular Films, and Shear Flow. U. Landman, W.D. Luedtke, J. Ouyang, J. Gao

9:45 - Tribology of Microelectromechanical Systems. M. Mehregany, J. Ramanaphan,

10:25 - Intermission

10:40 - Tribology of Amorphous Carbon Films (a:C and a:CH) by Computer Simulation. J.F. Belak, J.N. Glosli, M.R. Philpott

11:20 - Molecular Tribology of Hydrocarbon Systems. J.A. Harrison, M.D. Perry, R.J. Colton, C.T. White, D.W. Brenner

11:40 - Two-Dimensionally Quantized Friction Observed with Two-Dimensional Frictional Force Microscope. S. Fujisawa, E. Kishi, Y. Sugawara, S. Morita

Symposium on Molecular Tribology

Division of Colloid Chemistry and Surface Chemistry

American Chemical Society National Meeting

Wednesday Morning, April 5, 1995; Park Ballroom B

Chair: A. Gellman

9:00 - Noise, Scatter, and Fluctuation of Friction. A.L. Demirel, A. Dhinojwala, S. Granick

9:40 - Monte Carlo Calculations for the Mechanical Relaxation of a Self-Assembled Monolayer and for the Structures of Alkane/Metal Interfaces. J.I. Siepmann

10:00 - Effect of Solid Surface Energy and Pressure in Inducing Solid-Liquid Phase Transitions in Ultra-Thin N-Octane Films. R.K. Ballamudi, I.A. Bitsanis

10:20 - Intermission

10:40 - Molecular Structure of Organic Monolayers Under Compressive and Shear Forces. M. Salmeron

11:20 - Nano-Rheology of Molecularly-Thin Perfluoropolyether Lubricants. A.M. Homola, H.-W. Hu, D. Yoon, H. Brown

11:40 - Infrared Study of the Chemistry of Boundary Lubrication with High Temperature and High Pressure Shear. C. Westerfield, S.F. Agnew

Symposium on Molecular Tribology

Division of Colloid Chemistry and Surface Chemistry

American Chemical Society National Meeting

Wednesday Afternoon, April 5, 1995; Park Ballroom B

Chair: M. Salmeron

2:00 - Tribology Issues Encountered in Space Vehicles. M.R. Hilton

2:40 - Studies of the Surface Chemistry of Spacecraft Lubricant Additives on Bearing Materials. S.V. Didziulis, P.A. Bertrand

3:00 - Chemical Interaction of Organic Molecules with Fresh Metal Surfaces Formed under Tribological Conditions. S. Mori, Y. Shitara, J. Imai

3:20 - Intermission

3:40 - Effect of Surface Contamination on the UHV Friction Behavior of the Cu(111)/Cu(111) Interface. C.F. McFadden, A.J. Gellman

4:00 - A Novel UHV Surface Analysis Instrument for Studying Tribological Problems in Automotive Lubricant Applications. J.K. Mowlem

4:20 - Friction Modification for Improved Fuel Economy. H. Ohtani, R.J. Hartley, D.W. Stinnett, D.W. Smith

4:00 - Surface Chemistry of Chlorinated Hydrocarbon Lubricant Additives. W.T. Tysoe

Symposium on Molecular Tribology

Division of Colloid Chemistry and Surface Chemistry

American Chemical Society National Meeting

Thursday Morning, April 6, 1995; Park Ballroom B

Chair: S.S. Perry

9:00 - Electronic Contributions to Sliding Friction. J. Krim

9:40 - Application of Surface Science Concepts to Tribology. A.J. Gellman, C. McFadden, J. Meyers

10:20 - Intermission

10:40 - Contrast Mechanisms of Friction Force Microscopy. E. Meyer, R. Luthi, L. Howald, W. Gutmannsbauer, H.-J. Guntherodt

11:20 - Friction Force Microscopy in Ultrahigh Vacuum: A Study on C_{60} Thin Films Deposited on NaCl. R. Luthi, E. Meyer, H. Haefke, L. Howald, H.-J. Guntherodt

11:40 - AFM Studies of Corrosive Tribological Wear. S. Nakahara, J.T. Dickinson, S.C. Langford

Symposium on Molecular Tribology

Division of Colloid Chemistry and Surface Chemistry

American Chemical Society National Meeting

Thursday Afternoon; Park Ballroom B

Chair: A. Homola

2:00 - Tribochemical Issues at the Head/Disc Interface of a Rigid Disc Drive. B.Marchon

2:40 - Fluorescence Preceding and Accompanying Carbon Deposition in Silicon Nitride Friction Contacts Lubricated by Organic Vapors at High Temperatures. J.L. Lauer, V. Parbhakaran, R. Kodama, F.E. Talke

3:00 - Spreading Characteristics of Thin Films of Poly(perfluoroalkylether) Lubes on Solid Surfaces. B.G. Min, J.W. Choi, H.R. Brown, D.Y. Yoon, T.M. O'Connor, M.S. Jhon

3:20 - Intermission

3:40 - Nanotribology of Clean and Lubricated Amorphous Carbon Surfaces. S.S. Perry

4:20 - Tribological Studies in and on Lubricants with Atomic Force Microscopy. R.M. Overney, D.P. Leta, C.F. Pictroski, K.M. Creegan

4:40 - Probing Molecular Relaxation on Polymer Surfaces with Friction Force Microscopy. G.D. Haugstad, W.L. Gladfelter, E.B. Weberg, R.T. Weberg, R.R. Jones

Posters in Tuesday Evening Poster Session:

Anaheim Marriott, Northwest Hall

Friction Force Microscopy in Ultrahigh Vacuum: an Atomic Scale Study.

R. Lüthi, E. Meyer, H. Haefke, L. Howald, and H.-J. Güntherodt

Two-Dimensional Stick-Slip Model Combined with Effective Ahesive Radius.

S. Morita, S. Fujisawa, E. Kishi, Y. Sugawara

EXAFS Studies of the Structure of Sputter-Deposited MoS_2 Films.

J.R. Lince, M.R. Hilton, S.V. Didziulis

Molecular Design of Novel Lubricity Additives: Ortho-Phenylene Phosphates.

I. Minami

Luminescence and Mass Spectrometric Probes of Mechanical Damage in Ceramics.

J.T. Dickinson, R.L. Webb, L.C. Jensen

Electrical Conductivity Measurements of Polymer Thin Films on Metal Substrates.

J.T. Dickinson, L.C. Jensen

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INTERFACIAL JUNCTIONS, CONFINED MOLECULAR FILMS, AND SHEAR FLOW.

Uzi Landman, W. D. Luedtke, J. Ouyang, and J. Gao. School of Physics, Georgia Institute of Technology, Atlanta, Georgia 30332.

Atomic-scale interfacial structures, dynamics, response, and flow characteristics, occurring when two material bodies are brought into contact, separated or sheared with respect to each other, are of fundamental and practical interests. Computer-based molecular dynamics simulations, in conjunction with modern microscopies, allow investigations of such systems with high resolution. Topics which we discuss include: formation mechanisms, mechanical and electrical properties of intermetallic junctions; properties of confined molecular liquid films and liquid junctions; asperity-asperity collisions and wear during relative motion between two interfaces, and flow characteristics and transformations occurring in thin-film molecular lubricants during such interfacial shear processes.

Research supported by U. S. DOE, NSF, AFOSR.

ABSTRACT. Please be BRIEF—150 words maximum if possible. Title of paper should be ALL CAPS; author(s) listed by first name, middle initial, last name; indicate address w/zip code. SINGLE SPACE, BLACK INK.

A. DIVISION OF Colloids and Surface Chemistry

B. MEMBER ☐ Yes ☑ No

C. TITLE OF PAPER INTERFACIAL JUNCTIONS, CONFINED MOLECULAR FILMS, AND SHEAR FLOW.

(To be filled in by Division)
Paper number as listed on program _____

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TRIBOLOGY OF MICROELECTROMECHANICAL SYSTEMS. Mehran Mehregany, Department of Electrical Engineering & Applied Physics, Case Western Reserve University, Cleveland, Ohio 44106-7221

Recent advances of the microactuator technology are transforming the conventional field of solid-state transducers into what is increasingly becoming known as microelectromechanical systems (MEMS). In the most general form, MEMS would consist of mechanical elements, sensors, actuators, and electronics integrated in the same environment (e.g., on a silicon chip). MEMS bring about new capabilities for gathering information from the environment and in turn manipulating the environment for a desired goal. Since moving mechanical elements are an integral component of MEMS, tribological issues can play an important role in the performance of these micromechanical devices/systems. The presentation will include: (i) a short overview of MEMS; (ii) a discussion of when and where tribologial issues are important in MEMS; and (iii) a review of results from studies of friction and wear in micromechanical devices.

ABSTRACT. Please be BRIEF—150 words maximum if possible. Title of paper should be ALL CAPS; author(s) listed by first name, middle initial, last name; indicate address w/zip code. SINGLE SPACE, BLACK INK.

A. DIVISION OF

B. MEMBER ☐ Yes ☒ No

C. TITLE OF PAPER Tribology of Microelectromechanical Systems

Please indicate preference: X oral _____ poster

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TRIBOLOGY OF AMORPHOUS CARBON FILMS (a:C AND a:CH) BY COMPUTER SIMULATION.[1] James F. Belak and James N. Glosli, Lawrence Livermore National Laboratory, Livermore, CA 94550 and Michael R. Philpott, IBM Almaden Research Center, San Jose CA 95120-6099.

Ultra-thin amorphous carbon films approximately 20 nm thick are used as protective coatings on magnetic disk drives to prevent friction and wear. With future generation high density disks coatings as small as 5 nm are being called for. The structure and function of this family of coatings at the atomic level is poorly understood. To address this we have simulated the growth of a:C and a:CH films 1 to 10 nm thick using Brenner's bond-order potential with added torsional energy terms. The microstructure, though amorphous, shows a propensity towards graphitic structures at low deposition energy (<1eV) and towards higher density and diamond-like structures at higher deposition energy (>20eV). In this paper we present simulations of the distribution of stress and strain within these films and the evolution of the microstructure during a simulated indentation and sliding contact by a hard asperity.

1. Work performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under contract No. W-7405-ENG-48.

ABSTRACT. Please be BRIEF—150 words maximum if possible. Title of paper should be ALL CAPS; author(s) listed by first name, middle initial, last name; indicate address w/zip code. SINGLE SPACE, BLACK INK.

A. DIVISION OF Colloidal and Surface Science

B. MEMBER [X] Yes [ ] No

C. TITLE OF PAPER Tribology of Amorphous Carbon Films (a:C and a:CH) by Computer Simulation

(To be filled in by Division)
Paper number as listed on program _____

Please indicate preference: X oral _____ poster

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MOLECULAR TRIBOLOGY OF HYDROCARBON SYSTEMS. Judith A. Harrison, US Naval Academy, Chemistry Department, Annapolis, MD, 21402-5026, USA.

The development of new technological applications involving diamond coatings has accompanied recent advances in the chemical vapor deposition of diamond coatings. Since a great number of applications involving these films, which predominately show (111) and (100) facets, deal with the motion of diamond on diamond, understanding the tribological properties of these diamond facets is paramount. If the atomic-scale mechanisms which give rise to the observed tribological characteristics were understood, this knowledge might ultimately lead to the design of coatings with specific friction and wear properties. With this in mind, we have been using molecular dynamics to examine the atomic-scale phenomena which govern the friction and wear of diamond surfaces. These simulations have provided insight into the behavior of the friction coefficient as a function of load, temperature, sliding speed, and crystallographic sliding direction when two atomically-flat, hydrogen-terminated, diamond (111) surfaces are in sliding contact. Replacing some of the surface hydrogen atoms with other hydrocarbon groups makes the diamond surface rougher, and perhaps, more realistic. The frictional properties of these surfaces, the specific tribochemical reactions which occur when sliding, and the associated reaction mechanisms, have all been examined for these more realistic surfaces. More recently, we have examined the atomic-scale frictional properties of diamond (100)-(2x1) reconstructed surfaces. Our results to date, for both diamond (100) and (111) will be summarized in this talk.

ABSTRACT. Please be BRIEF—150 words maximum if possible. Title of paper should be ALL CAPS; author(s) listed by first name, middle initial, last name; indicate address w/zip code. SINGLE SPACE, BLACK INK.

A. DIVISION OF

B. MEMBER ☒ XX Yes ☐ No

C. TITLE OF PAPER

MOLECULAR TRIBOLOGY OF HYDROCARBON SYSTEMS

Please indicate preference: XX oral _____ poster

(To be filled in by Division)
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TWO-DIMENSIONALLY QUANTIZED FRICTION OBSERVED WITH TWO-DIMENSIONAL FRICTIONAL FORCE MICROSCOPE

Satoru Fujisawa, Eigo Kishi, Yasuhiro Sugawara, and Seizo Morita,
Department of Physics, Faculty of Science, Hiroshima University,
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We investigated a two-dimensional nature of atomic scale friction between a AFM tip of single asperity and atomically flat surfaces, where frictional force becomes two-dimensional vector. As the atomically flat surface, we used non-layered materials such as NaF as well as layered materials. Using two-dimensional frictional force microscope which detects both components of the two-dimensional frictional force vector separately and simultaneously, we found that the single asperity shows the two-dimensionally quantized jump with the lattice periodicity of the atomically flat surfaces. This phenomenon is explained by "two-dimensional stick-slip" model quantitatively with "lateral force curve" calibration. We also found that this quantized behavior shows fluctuation. These phenomena show that on an atomic scale the frictional force is quantized two-dimensionally and acts not only along but also across the scan direction, although it is contradictory to assumption of the macroscopic friction.

ABSTRACT. Please be BRIEF—150 words maximum if possible. Title of paper should be ALL CAPS; author(s) listed by first name, middle initial, last name; indicate address w/zip code. SINGLE SPACE, BLACK INK.

A. DIVISION OF Surface Physics

B. MEMBER ☐ Yes ☒ No

C. TITLE OF PAPER

Two-Dimensionally Quantized Friction Observed with Two-Dimensional Frictional Force Microscope

Please indicate preference: ___✓___ oral _____ poster

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NOISE, SCATTER, AND FLUCTUATION OF FRICTION. A. Levent Demirel, Ali Dhinojwala, and Steve Granick, Materials Research Laboratory, University of Illinois, Urbana, IL 61801.

The confinement-induced solidity in lubricant boundary layers gives way, under external drive, to a kinetic sliding state in which the viscous dissipation is essentially velocity-independent but with giant fluctuations. These fluctuations increase gradually over many successive periods of stick-slip and decrease abruptly; the form is triangulation spikes on a constant baseline. The statistical average of the number and amplitude of spikes increases systematically with decreasing drive amplitude, but always with superposed noise and fluctuation that cannot be explained from classical considerations of apparatus stiffness. We conclude that the liquid formed structure at a constant rate and snapped suddenly so that observed stress reflected a competition between equilibration tendencies and imposed shear drive. In this way, patterns of noise and fluctuation were analyzed quantitatively.

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A. DIVISION OF

B. MEMBER ☐ Yes ☐ No

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Paper number as listed on program _____

C. TITLE OF PAPER

Noise, Scatter & Fluctuation of Friction

Please indicate preference: _____ oral _____ poster

D. AUTHORS Al Levent Demirel, A. Dhinojwala, Steve Granick

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NANO-RHEOLOGY OF MOLECULARLY-THIN PERFLUOROPOLYETHER LUBRICANTS.

A.M. Homola, H-W. Hu, D. Yoon and H. Brown, IBM Research Division, Almaden Research Center, San Jose, California 95120-6099

The sliding experiments were performed with the Surface Force Apparatus using narrow molecular weight fractions of perfluoropolyether melt. This class of materials is currently almost exclusively used in the computer industry as lubricants for memory disks. During a typical sliding experiment, in which the direction of sliding was reversed with each sliding cycle, the polymeric film exhibited a pronounced shear thinning behavior with the kinetic friction decreasing gradually over many minutes. After a rest time, commencement of sliding was manifested by a sharp frictional peak representing the yield stress, which increased in magnitude with duration of rest. With increasing rest time, polymer molecules assumed their original configurations with relaxation time of the order of several hours. Increase in sliding velocities resulted in a higher degree of molecular alignment and, following commencement of sliding, in a reduced tendency to relax. Thinner films showed a considerably lower rate of shear thinning than the thicker ones indicating an influence of the substrate on the molecular configurations and rheology of these films. With increasing molecular weight, from 2,000 to 11,000, polymeric films exhibited increasingly higher frictional dependency on shearing time and showed increasingly longer relaxation time. These experiments are contrasted with results obtained with a pin-on-disk apparatus in which sliding conditions are closer to a real system.

ABSTRACT. Please be BRIEF—150 words maximum if possible. Title of paper should be ALL CAPS; author(s) listed by first name, middle initial, last name; indicate address w/zip code. SINGLE SPACE, BLACK INK.

A. DIVISION OF Colloid and Surface Chemistry

B. MEMBER ☒ Yes ☐ No

C. TITLE OF PAPER
Nano-Rheology of Molecularly-Thin Perfluoropolyether Lubricants

Please indicate preference: V oral _____ poster

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EFFECT OF SOLID SURFACE ENERGY AND PRESSURE IN INDUCING SOLID-LIQUID PHASE TRANSITIONS IN ULTRA-THIN N-OCTANE FILMS. Ravi K. Ballamudi and Ioannis A. Bitsanis, Department of Chemical Engineering, University of Florida, Gainesville, Florida 32611

In this work we present the results of several molecular dynamics studies of molecularly thin (3 methylene segments wide) n-octane films confined between topographically smooth solid surfaces. The dependence of film characteristics on increasing solid-methylene segment energetic affinity and film pressure were investigated. Our simulations showed an abrupt transition of the molecules at a critical solid-methylene unit energetic affinity. This transition was signalled by a discontinuous jump in the intermolecular order and a precipitous extension of the octane molecules. The transition was accompanied by the freezing of large scale translational and rotational motions. Several pressures of the system were studied by adjusting the film thickness to a number of different values. The film undergoes a liquid to solid phase transition with decreasing film thickness. This transition is evident from the sudden change in the intermolecular order and the cessation of translational and rotational motion. Furthermore, both (energy driven and pressure driven) transitions are from a strongly organized liquid to a "granular" or "polycrystalline" solid. Our simulations provide a natural explanation to the solid like features observed in several experiments.

ABSTRACT. Please be BRIEF—150 words maximum if possible. Title of paper should be ALL CAPS; author(s) listed by first name, middle initial, last name; indicate address w/zip code. SINGLE SPACE, BLACK INK.

A. DIVISION OF MOLECULAR TRIBOLOGY

B. MEMBER [X] Yes [ ] No

C. TITLE OF PAPER

Effect of Solid Surface Energy and Pressure in Inducing Solid-Liquid Phase Transitions in Ultra-Thin N-Octane Films

Please indicate preference: ____X____ oral _____ poster

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G. For contributed papers, do authors meet criteria outlined in ACS Bylaw VI, Section 6(3)? See instructions.

[X] Yes [ ] No

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MOLECULAR STRUCTURE OF ORGANIC MONOLAYERS UNDER COMPRESSIVE AND SHEAR FORCES. M. Salmeron. Materials Science Division. Lawrence Berkeley Laboratory. Berkeley, CA 94720.

The Atomic Force Microscope (AFM) and the Surface Forces Apparatus were used to study the structure of self-assembled and Langmuir-Blodgett monolayers on Au(111), glass and mica surfaces when subjected to external forces. At pressures of ~100 MPa, the -CH3 and -OH terminal groups become disordered as determined by *in situ* spectroscopy using non-linear optical techniques (SHG, SFG). AFM studies of thiols on Au(111) revealed that the layers maintain an ordered arrangement of the *rotationally averaged* molecular chain, for pressures below a critical value (0.5 to 1 GPa). At this point, a reversible disordering-displacement transition takes place where the tip images the atomic periodicity of the Au substrate. The friction force experiences a dramatic change across the critical transition.

ABSTRACT. Please be BRIEF—150 words maximum if possible. Title of paper should be ALL CAPS; author(s) listed by first name, middle initial, last name; indicate address w/zip code. SINGLE SPACE, BLACK INK.

A. DIVISION OF Colloid & Surface Science

B. MEMBER [X] Yes [ ] No

C. TITLE OF PAPER Molecular Structure of Organic Monolayers Under Compressive and Shear Forces

Please indicate preference: X oral _____ poster

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MONTE CARLO CALCULATIONS FOR THE MECHANICAL RELAXATION OF A SELF-ASSEMBLED MONOLAYER AND FOR THE STRUCTURES OF ALKANE/METAL INTERFACES. J. Ilja Siepmann, Department of Chemistry, University of Minnesota, 207 Pleasant St. SE, Minneapolis, MN 55455.

The Monte Carlo approach has the advantage that it allows us to design moves which sample slow transformations efficiently and thereby enables simulations for systems which might not be readily amenable to conventional simulation techniques. Configurational-bias Monte Carlo calculations have been used to study the mechanical relaxation of a monolayer of $CH_3(CH_2)_{15}$ adsorbed molecules on a gold substrate when subjected to indentation by a nanometer-scale force-microscope tip. An almost elastic response is observed to forces that compress the monolayer by about 25% of its original thickness. Compression leads to very substantial but reversible changes in the tilt angle and the conformation of the molecules. The same Monte Carlo technique has been used to probe the structural properties of liquid alkane films of various thicknesses in contact with a flat metal substrate.

ABSTRACT. Please be BRIEF—150 words maximum if possible. Title of paper should be ALL CAPS; author(s) listed by first name, middle initial, last name; indicate address w/zip code. SINGLE SPACE, BLACK INK.

A. DIVISION OF Colloid and Surface Chemistry

B. MEMBER ☒ Yes ☐ No

C. TITLE OF PAPER
Monte Carlo Calculations for the Mechanical Relaxation of a Self-Assembled Monolayer and for the Structures of Alkane/Metal Interfaces

Please indicate preference: X oral _____ poster

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Infrared Study of the Chemistry of Boundary Lubrication with High Temperature and High Pressure Shear, Curtis Westerfield and Stephen F. Agnew, Chemical Science and Technology, Los Alamos National Laboratory,Los Alamos, NM 87545.

A unique diamond anvil cell has been constructed which permits the spectroscopic study of boundary layers under conditions of high temperature, high pressure, and shear. We have used this cell in combination with FTIR spectroscopy to probe the function of stearic acid and zinc dialkyl-dithiophosphate (ZnDDP) as boundary layer enhancers. We have shown that thick boundary layers (~1 μm) of stearic acid continue to exist at pressures as high as 5.0 GPa (725,000 psig). We have also demonstrated that the decomposition of ZnDDP in mineral oil under static high pressure and high temperature is first enhanced by increasing pressure, reaching a maximum at ~0.7 GPa (~10,000 psig), and is thereafter retarded by further increases in pressure. This result suggests that the decomposition of ZnDDP is triggered by pressure increases associated with boundary lubrication, rather than frictional heating.

ABSTRACT. Please be BRIEF—150 words maximum if possible. Title of paper should be ALL CAPS; author(s) listed by first name, middle initial, last name; indicate address w/zip code. SINGLE SPACE, BLACK INK.

A. DIVISION OF Colloid and Surface Chemistry

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B. MEMBER [x] Yes [ ] No

C. TITLE OF PAPER Infarared Study of the Chemistry of Boundary Lubrication with High Temperature and High Pressure Shear

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TRIBOLOGY ISSUES ENCOUNTERED IN SPACE VEHICLES, M. R. Hilton, Mechanics and Materials Technology Center, The Aerospace Corporation, El Segundo, CA 90245-4691

The proper lubrication of mechanical devices is a critical aspect of the successful operation of spacecraft. Within the last decade, an increased level of understanding of the fundamental aspects of chemical and mechanical interactions of tribomaterials for spacecraft applications has been achieved. This knowledge has precipitated significant changes in lubricant and lubricant additive selection. This presentation will discuss the tribological design issues of spacecraft systems, with particular emphasis on atomic- and nanometer-scale interactions. The properties of solid and fluid lubricants, and of lubricant additives will be reviewed. Lubricant interactions with surfaces will be discussed.

ABSTRACT. Please be BRIEF—150 words maximum if possible. Title of paper should be ALL CAPS; author(s) listed by first name, middle initial, last name; indicate address w/zip code. SINGLE SPACE, BLACK INK.

A. DIVISION OF Colloid and Surface Chemistry

B. MEMBER ☐ Yes ☒ No Invited

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STUDIES OF THE SURFACE CHEMISTRY OF SPACECRAFT LUBRICANT ADDITIVES ON BEARING MATERIALS, S. V. Didziulis and P. A. Bertrand, Surface Science Department, Mechanics and Materials Technology Center, The Aerospace Corporation, El Segundo, CA 90245.

The successful operation of liquid lubricated spacecraft mechanisms is often dependent on the performance of the boundary additives included with the lubricant to lower friction and limit wear. The two most widely used additives for space are tricresyl phosphate (TCP - and related phosphate esters) and lead naphthenate (Pbnp). For these additives to function properly, they must interact with the bearing material surfaces in the mechanical contact, and this chemistry is highly dependent on the substrate material. In this work, we will present spectroscopic analyses of the additive and surface-additive reaction products after treating a variety of bearing material samples (including steels, silicon ceramics, and TiC and TiN materials) with additive-containing solutions. Studies include infrared analyses of additive solutions, and Auger and XPS studies of the substrate surfaces. The relative effectiveness of bearing pretreatments with additives versus inclusion of the additive in the lubricant will be discussed.

ABSTRACT. Please be BRIEF—150 words maximum if possible. Title of paper should be ALL CAPS; author(s) listed by first name, middle initial, last name; indicate address w/zip code. SINGLE SPACE, BLACK INK.

A. DIVISION OF Colloid and Surface Chemistry

B. MEMBER [xx] Yes [ ] No

C. TITLE OF PAPER Studies of the Surface Chemistry of Spacecraft Lubricant Additives on Bearing Materials.

Please indicate preference: xx oral _____ poster

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CHEMICAL INTERACTION OF ORGANIC MOLECULES WITH FRESH METAL SURFACES FORMED UNDER TRIBOLOGICAL CONDITIONS, Shigeyuki Mori, Yuji Shitara and Jun Imai, Department of Applied Chemistry and Molecular Science, Iwate University, Morioka, Japan 020

Fresh surfaces were formed by scratching under high vacuum conditions. Chemisorption and surface reactions were monitored with a quadrupole mass spectrometer. Fresh surface of gold was so active that organic compounds chemisorb on it and some decomposition reactions were observed even at room temperature. Chemical properties of fresh surfaces of 11 to 14-group metals such as Cu, Ag, Au, Zn, Al, Sn and Pb were found to be dependent on their electronic structures. Although aromatic compounds and olefins chemisorbed on fresh surfaces of Cu and Au, they did not chemisorb on those of Zn, Al and Sn. The result indicates that fresh surfaces of Cu and Au show a similar chemical property as transition metal. Organic compounds containing oxygen such as alcohols and esters easily chemisorbed on fresh surfaces of 11 to 13-group metals. However, fresh surface has no activity for chemisorption of organic compounds.

ABSTRACT. Please be BRIEF—150 words maximum if possible. Title of paper should be ALL CAPS; author(s) listed by first name, middle initial, last name; indicate address w/zip code. SINGLE SPACE, BLACK INK.

A. DIVISION OF Symposium on Molecular Tribology

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C. TITLE OF PAPER
CHEMICAL INTERACTION OF ORGANIC MOLECULES WITH FRESH METAL SURFACES FORMED UNDER TRIBOLOGICAL CONDITIONS

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[A.] DIVISION OF Colloid and Surface Chemistry

[B.] TITLE OF PAPER

Time Required for Presentation 15-20

Poster Presentation Preferred

Effect of Surface Contamination on the UHV Friction Behavior of the Cu(111)/Cu(111) Interface

on program _____

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Underline name of speaker

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Division Member? ☒ Yes ☐ No

[F.] American Chemist or Chemical Engineer?
If not, give classification such as biologist, physicist, etc. Ph.D.?
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☐ Chemical Engineer
Other _____

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Title The Adsorption of Enantiomeric Alcohols on "Chiral" Metal Surfaces Division Surf / Coll

[K.] ABSTRACT: Please be BRIEF—150 words maximum if possible. Title of paper should be ALL CAPS; author(s) listed by first name middle initial, last name; indicate full address w/zip code. SINGLE SPACE, BLACK CARBON RIBBON.

EFFECT OF SURFACE CONTAMINATION ON THE UHV FRICTION BEHAVIOR OF THE CU(111)/CU(111) INTERFACE. Christopher F. McFadden, Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL 61801. Andrew J. Gellman, Department of Chemical Engineering, Carnegie Mellon University, Pittsburgh, PA 15213.

An ultrahigh vacuum (UHV) tribometer has been used to study the tribological behavior of two Cu(111) surfaces modified with controlled levels of surface contamination in the form of carbon and sulfur. The tribometer is designed such that both Cu(111) samples may be prepared, characterized using auger electron spectroscopy (AES) and low energy electron diffraction (LEED), and brought into sliding contact all under UHV without exposure to the atmosphere. The shearing behavior of *clean* Cu(111) surfaces is characterized by high, erratic friction coefficients ($\mu_s = 4.6 \pm 1.1$). For modified surfaces the friction coefficient decreases monotonically with increasing, submonolayer coverages of carbon and sulfur. This sensitivity to trace levels of atomic adsorbates is in stark contrast with the lubricating ability of molecular adsorbates of ethanol and trifluoroethanol, which have no influence on the friction coefficient until coverages exceeding one monolayer. This suggests that the lubrication of metallic interfaces may not result from the presence of intact molecular species but instead from that of inorganic films formed during lubricant decomposition.

[L.] MAIL ABSTRACT TO PERSON NAMED IN ACS DIVISIONAL DEADLINES PUBLISHED (JUNE & DEC.) IN C&EN

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A NOVEL UHV SURFACE ANALYSIS INSTRUMENT FOR STUDYING TRIBOLOGICAL PROBLEMS IN AUTOMOTIVE LUBRICANT APPLICATIONS.

James K. Mowlem, Texaco Research and Development Department, P.O. Box 509, Beacon, New York 12508.

A surface analysis system comprising several UHV techniques (AES, XPS, UPS, SIMS, HREELS, and TPD) and a vacuum-compatible tribometer has been designed to investigate lubricant systems under "real-world" conditions within one instrument. Some of the unique features of this instrument are: a load-lock cell for quick sample exchange, and a high-pressure tribocell where friction experiments can be performed under high pressures (up to 5 atm.) of typical combustion gases (CO, NO, etc.) with subsequent surface spectroscopic characterization occurring without exposure to atmosphere. This enables one to acquire a more thorough understanding of chemisorption processes of complex molecular adsorption systems, and the tribological properties associated with these systems. Instrument features will be highlighted with discussion of results from model lubricant adsorption systems.

ABSTRACT. Please be BRIEF—150 words maximum if possible. Title of paper should be ALL CAPS; author(s) listed by first name, middle initial, last name; indicate address w/zip code. SINGLE SPACE, BLACK INK.

A. DIVISION OF Colloid and Surface Chemistry

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C. TITLE OF PAPER
A NOVEL UHV SURFACE ANALYSIS INSTRUMENT FOR STUDYING TRIBOLOGICAL PROBLEMS IN AUTOMOTIVE LUBRICANT APPLICATIONS

Please indicate preference: ___X___ oral _____ poster

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FRICTION MODIFICATION FOR IMPROVED FUEL ECONOMY. H. Ohtani*, R.J. Hartley, D.W. Stinnett, and D.W. Smith, Ethyl Research Center, Richmond, Virginia 23219, *Catalysis Research Center, Hokkaido University, Sapporo 060 JAPAN

ATF (automatic transmission fluid) is a multi-component multi-functional lubricant which controls frictional characteristics and durability of ATs (automatic transmissions)[1]. There is worldwide activity to develop ATs incorporating CSTCC (continuous slip torque converter clutch) design in order to improve fuel economy. Friction performance of ATFs is a key to successful implementation of this technology [2]. This paper reviews the frictional characteristics required for future ATFs, various friction tests using actual clutch materials, and the friction control techniques using oil-soluble friction modifying reagents. The possibility of utilizing modern surface science techniques in this field will be discussed. [1] A.G. Papay, Lubr. Engr. 39(7) (1983) 419. [2] H. Ohtani, R.J. Hartley, and D.W. Stinnett, SAE Paper 940821 (1994).

ABSTRACT. Please be BRIEF—150 words maximum if possible. Title of paper should be ALL CAPS; author(s) listed by first name, middle initial, last name; indicate address w/zip code. SINGLE SPACE, BLACK INK.

A. DIVISION OF Colloid and Surface Science

B. MEMBER [X] Yes [ ] No

C. TITLE OF PAPER

Friction Modification for Improved Fuel Economy

Please indicate preference: __X__ oral _____ poster

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SURFACE CHEMISTRY OF CHLORINATED HYDROCARBON LUBRICANT ADDITIVES.

W.T. Tysoe, Department of Chemistry and Laboratory for Surface Studies, University of Wisconsin-Milwaukee, WI 53211

Lubricant additives operating under extreme pressure (EP) conditions generally consist of a base fluid and contain additives which improve their tribological behavior. The most common of these additives are chlorinated hydrocarbons but are being replaced by other sulfur- or phosphorus-containing compounds. In order to understand the chemistry of these additives we have studied the tribological behavior of chlorinated hydrocarbons and find that they function (at relatively low applied loads) by thermally decomposing at the hot interface to form a lubricant layer that consists of an iron halide and which incorporates small carbon particles. At higher applied loads, the interfacial temperature exceeds the melting point of $FeCl_2$ so that this can no longer function as a lubricant layer. Under suitable conditions, notably when CCl_4 is used as additive, an iron carbide forms the anti-seizure layer.

ABSTRACT. Please be BRIEF—150 words maximum if possible. Title of paper should be ALL CAPS; author(s) listed by first name, middle initial, last name; indicate address w/zip code. SINGLE SPACE, BLACK INK.

A. DIVISION OF Colloids and Surfaces

B. MEMBER [X] Yes [ ] No

C. TITLE OF PAPER Surface Chemistry of Chlorinated Hydrocarbon Lubricant Additives

(To be filled in by Division)
Paper number as listed on program _____

Please indicate preference: X oral _____ poster

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ELECTRONIC CONTRIBUTIONS TO SLIDING FRICTION,* J. Krim,

Northeastern University, Boston, MA 02115

We have employed a quartz crystal microbalance (QCM) technique to measure sliding friction levels for simple molecular layers adsorbed on Ag and Ni surfaces. The QCM technique involves monitoring the degree to which adsorbed layers can track the oscillatory motion of the microbalance's electrode, which is directly dependent on the interfacial friction. We have studied the dependencies of the observed friction levels on the electrical conductivity of the QCM electrode as well as the phase (liquid or solid) and thickness of the adsorbed layer. We observe that both phononic [1,2] and electronic [3] mechanisms contribute to the energy dissipation, and describe our efforts to determine the relative importance of the electronic contributions. * In collaboration with C. Daly, A. Dayo and C. Mak. Work supported by NSF Grant DMR 9204022

[1] J.B. Sokoloff, Phys. Rev. B **47**, 6106 (1993)

[2] M. Cieplak, E.D. Smith, and M.O. Robbins, Science **265**, 1209 (1994)

[3] B.N.J. Persson, Phys. Rev. B 44, 3277 (1991)

ABSTRACT. Please be BRIEF—150 words maximum if possible. Title of paper should be ALL CAPS; author(s) listed by first name, middle initial, last name; indicate address w/zip code. SINGLE SPACE, BLACK INK.

A. DIVISION OF Colloid and Surface Chemistry

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C. TITLE OF PAPER Electronic Contributions to Sliding Friction

(To be filled in by Division)
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APPLICATION OF SURFACE SCIENCE CONCEPTS TO TRIBOLOGY.

Andrew J. Gellman, Chris McFadden, Jerry Meyers, Dept. of Chemical Eng.
Carnegie Mellon University, Pittsburgh, PA 15213

Recent progress in the application of surface science approaches to the study of tribology have been in the areas of lubricant surface chemistry and in understanding the tribological properties of metal-metal interfaces sliding under the highly controlled conditions of ultra-high vacuum. Our study of fluorinated ethers, alcohols and acids on metal surfaces has enabled us to understand some of the decomposition mechanisms that lead to their destruction and ultimate failure as lubricants. Systematic comparison of the surface chemistry of these fluorocarbons with their hydorcarbons analogues has brought to light the effects that flourine can have on the kinetics of surface reactions and the role that fluorination has in increasing the thermal stability of these species on metal surfaces. Parallel measurement of the tribological properties of metal-metal interfaces lubricated by molecular monolayers reveals the characteristics of adsorbed films required for effective lubrication.

[A.] DIVISION OF Colloid and Surface Science

[B.] MEMBER [X] Yes [ ] No

[C.] TITLE OF PAPER

Application of Surface Science Concepts to Tribology

Please indicate preference: __X__ oral _____ poster

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CONTRAST MECHANISMS OF FRICTION FORCE MICROSCOPY

E. Meyer, R. Lüthi, L. Howald, W. Gutmannsbauer and H.-J. Güntherodt, Institute of Physics, Condensed Matter Division, Klingelbergstr. 32, 4056 Basel
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Friction force microscopy experiments are performed in well-defined environments, such as ultrahigh vacuum, dried nitrogen and various vapors. Based upon experimental evidences, the mechanisms of contrast formation of friction on the nanometer-scale, including the role of water films, are discussed.

ABSTRACT. Please be BRIEF—150 words maximum if possible. Title of paper should be ALL CAPS; author(s) listed by first name, middle initial, last name; indicate address w/zip code. SINGLE SPACE, BLACK INK.

A. DIVISION OF Symposium on "Molecular Tribology"

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B. MEMBER ☐ Yes ☒ No

C. TITLE OF PAPER
Contrast Mechanisms of Friction Force Microscopy

Please indicate preference: ___(invited)___ oral _____ poster

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FRICTION FORCE MICROSCOPY IN ULTRAHIGH VACUUM: A STUDY ON C_{60} THIN FILMS DEPOSITED ON NaCl

R. Lüthi, E. Meyer, H. Haefke, L. Howald and H.-J. Güntherodt, Institute of Physics, Condensed Matter Div., Experimental Physics, University of Basel, CH-4056 Basel,)

We present a "nanosled" experiment performed in ultrahigh vacuum with a scanning force microscope. Islands of C_{60}, deposited on NaCl(001), were moved by the action of the probing tip in a controlled way. The dissipation and cohesive energies of C_{60} as well as the shear strength could be determined quantitatively in these nanometer-scale experiments. Furthermore, the tribological properties (friction coefficient and initial stage of wear) are discussed by means of the two-dimensional histogram technique.

ABSTRACT. Please be BRIEF—150 words maximum if possible. Title of paper should be ALL CAPS; author(s) listed by first name, middle initial, last name; indicate address w/zip code. SINGLE SPACE, BLACK INK.

A. DIVISION OF Symposium on „molecular tribology"

B. MEMBER ☐ Yes ☒ No

C. TITLE OF PAPER Friction Force Microscopy: A study on C_{60} thin films deposited on NaCl

(To be filled in by Division)
Paper number as listed on program _____

Please indicate preference: X oral _____ poster

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AFM STUDIES OF CORROSIVE TRIBOLOGICAL WEAR.* Sumio Nakahara, J. Thomas Dickinson, and Stephen C. Langford, Washington State University, Pullman, WA 99164-2814

The combination of simultaneous tribological loading *and* corrosive chemical exposure can dramatically enhance wear. A model system for study of such effects is a hydrophilic inorganic single crystal in a humid atmosphere, here single crystal $NaNO_3$. We have modified our AFM to permit measured variations in relative humidity (RH) during scanning. Abrasion is performed with the AFM tip at normal loads (F_N) from 1-30 nN and tip velocities from 1-200 μm/s. Freshly cleaved crystals exhibit 6 Å steps, corresponding to two unit cells, which are stable under repeated scanning. At high humidity, a few scans at low normal forces show clear step dissolution at typical velocities of 100 nm/s. Additional scanning at RH>40% produces dramatic mechanically stimulated corrosive attack. At slightly higher F_N we observe the formation of moguls due to cooperative tip-materials interactions. We present the influence of F_N, tip velocity, and RH on the rate of corrosive wear and discuss models for the observed structures. *This work supported by the National Science Foundation.

Division of ~~Chemical Physics~~ Colloid and Surface Chemistry

Member: **Yes** No

Title of Paper: AFM STUDIES OF CORROSIVE TRIBOLOGICAL WEAR

Please indicate preference: **Oral** Poster

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TRIBOCHEMICAL ISSUES AT THE HEAD/DISC INTERFACE OF A RIGID DISC DRIVE. B. Marchon, Seagate Technology, Fremont, CA 94538.

This paper reviews various chemical reactions that can be tribologically induced at a head/disc interface of a rigid disc drive during sliding contacts. A typical film structure for a thin film disc involves 30-80nm of cobalt alloy, 15-30nm of wear resistant overcoat, and 1-3nm of liquid lubricant. Head are flying at heights in the 20-100nm range, with velocities in the 10-30 m/s range. Given the nanometer-scale of the film structure, it is intuitive that most of the non-catastrophic wear processes must be chemical in nature. Tribochemical (corrosive) wear of some amorphous carbon overcoat in oxygen is one of the mechanisms that have been proposed earlier to account for friction buildup during sliding. More recently, several groups have shown direct evidence for this type of tribochemically-induced reaction. Also, a number of papers have focussed on the chemical degradation of the lubricant film during sliding. This talk will attempt to review these issues, and it will focus on general trends in the rigid disc industry, as the head-disc separation will eventually vanish.

ABSTRACT. Please be BRIEF—150 words maximum if possible. Title of paper should be ALL CAPS; author(s) listed by first name, middle initial, last name; indicate address w/zip code. SINGLE SPACE, BLACK INK.

A. DIVISION OF Colloid and Surface Chemistry

B. MEMBER ☐ Yes ☒ No

C. TITLE OF PAPER

TRIBOCHEMICAL ISSUES AT THE HEAD/DISC INTERFACE OF A RIGID DISC DRIVE

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EFFECTS OF GAS COMPOSITION, HUMIDITY AND TEMPERATURE ON THE TRIBOLOGY OF THE HEAD/DISK INTERFACE. M. Yang, J. L. Lauer and F.E. Talke, Center for Magnetic Recording Research, University of California, San Diego, La Jolla, California 92093-0401

Slider-on-disk drag tests conducted in a specially designed environmental chamber have shown that a relative humidity above 2% in the environmental gases was a more important factor determining friction in computer disk drives than oxygen/nitrogen ratio, carbon dioxide content and even global temperature, as long as carbon overcoats but no lubricants were used. But when lubricants were present in the interface, they determined friction. At relative humidities below 2% a higher oxygen content was somewhat effective in prolonging time-to-failure in air, but an atmosphere of essentially only carbon dioxide was more effective. Possible reasons could be a shift of the carbon/oxygen/carbon dioxide equilibrium and reduction of the interface temperature as more heat is absorbed in a given volume by carbon dioxide than by diatomic gases.

ABSTRACT. Please be BRIEF—150 words maximum if possible. Title of paper should be ALL CAPS; author(s) listed by first name, middle initial, last name; indicate address w/zip code. SINGLE SPACE, BLACK INK.

A. DIVISION OF Colloid and Surface Chemistry

B. MEMBER [X] Yes [ ] No

C. TITLE OF PAPER Effects of Gas Composition, Humidity and Temperature on the Tribology of the Head/Disk Interface

Please indicate preference: x oral _____ poster

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SPREADING CHARACTERISTICS OF THIN FILMS OF POLY(PERFLUOROALKYLETHER) LUBES ON SOLID SURFACES. B. G. Min, J. W. Choi, H. R. Brown, D. Y. Yoon, IBM Research Division, Almaden Research Center, San Jose, CA 95120; T. M. O'Connor, and M. S. Jhon, Carnegie Mellon University, Pittsburgh, PA 15213

The spreading characteristics of poly(perfluoroalkylether), a random copolymer of CF_2O and CF_2CF_2O moieties, on solid surfaces have been investigated with a scanning micro-ellipsometer as function of film thickness, molecular weight, chain-end functionality, and relative humidity. Spreading of the polymer with no functional chain ends (Z-15) occurs mainly by the diffusion-like movement of the fast moving front of less than 10 Å in thickness. The apparent diffusion constant of this front is nearly independent of the initial film thickness (>20 Å), and decreases with increasing molecular weight. The polymer with OH groups at both chain ends (Z-Dol) is found to spread by forming an apparent mono-molecular layer, which separates out from the initial film layer with a sharp boundary, with its thickness increasing with molecular weight. The apparent diffusion constant of Z-Dol is much smaller than that for Z-15 at the same molecular weight under inert atmosphere, but exhibits a dramatic increase under high relative humidity while Z-15 shows only a minor change with humidity. The effects of different solid surfaces and functional chain ends will also be discussed.

ABSTRACT. Please be BRIEF—150 words maximum if possible. Title of paper should be ALL CAPS; author(s) listed by first name, middle initial, last name; indicate address w/zip code. SINGLE SPACE, BLACK INK.

A. DIVISION OF Colloid and Surface Chemistry

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C. TITLE OF PAPER
Spreading characteristics of poly(perfluoroalkylether) lubes on solid surfaces

Please indicate preference: ✓ oral _____ poster

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NANOTRIBOLOGY OF CLEAN AND LUBRICATED AMORPHOUS CARBON SURFACES. Scott S. Perry, Department of Chemistry, University of Houston, Houston, TX 77204-5641

The tribological properties of amorphous carbon films have been investigated as a function of film composition and surface chemical modification. Carbon films are currently used as protective hard coatings in many applications, including computer disk drives, where control over friction and adhesion at the carbon surface is required. In these studies, atomic force microscopy (AFM) has been used to probe these properties on the nanometer or molecular scale. Adhesive forces between tip and surface have been determined through force-distance measurements, normalizing measurements between samples through a series of electrostatic measurements. Coefficients of friction have been calculated from simultaneous measurements of friction forces and applied loads. These measurements have been performed for carbon films with a range of hydrogen concentrations and surface treatments. Surface modifications have included surface oxidation as well as the addition of a lubricant species.

ABSTRACT. Please be BRIEF—150 words maximum if possible. Title of paper should be ALL CAPS; author(s) listed by first name, middle initial, last name; indicate address w/zip code. SINGLE SPACE, BLACK INK.

A. DIVISION OF ~~Physical Chemistry~~ Colloid and Surface Chemistry

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C. TITLE OF PAPER Nanotribology of Clean and Lubricated Amorphous Carbon Surfaces

Please indicate preference: x oral _____ poster

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TRIBOLOGICAL STUDIES IN AND ON LUBRICANTS WITH ATOMIC FORCE MICROSCOPY.

R.M. Overney, D.P. Leta, C.F. Pictroski, K.M. Creegan, Exxon Research and Engineering Company Annandale, NJ 08801

An atomic force microscopy study is presented on thin organic lubricant films and on lubricant fluids under confinement with solid interfaces. Local elastic compliance has been measured simultaneously with both topography and friction on the molecular scale of an organic bilayer assembly. The anisotropic and highly ordered structure of a lipid bilayer [1] caused contrast information in compliance measurements with asymmetric contact zones [2]. Physical properties of liquids such as the viscosity have been measured dependent on the distance to solid interfaces and compared with the fluid bulk viscosities. Finally, initial comparative tribological experiments between atomic force microscopy and surface forces apparatus will be reported.

[1] R.M. Overney et al., *Phys. Rev. Lett.* **72**, 3546 (1994).
[2] R.M. Overney et al., *Europhys. Lett.* **26**, 443 (1994).

ABSTRACT. Please be BRIEF—150 words maximum if possible. Title of paper should be ALL CAPS; author(s) listed by first name, middle initial, last name; indicate address w/zip code. SINGLE SPACE, BLACK INK.

A. DIVISION OF Colloid & Surface Chemistry

B. MEMBER ☒ Yes ☐ No

C. TITLE OF PAPER Tribological Studies in and on lubricants with atomic force microscopy

Please indicate preference: X oral _____ poster

D. AUTHORS R.M. Overney, D.P. Leta, C.F. Pictroski, K.M. Creegan

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PROBING MOLECULAR RELAXATION ON POLYMER SURFACES WITH FRICTION FORCE MICROSCOPY. Greg D. Haugstad, Center for Interfacial Engineering, University of Minnesota, Minneapolis, Minnesota 55455; Wayne L. Gladfelter, Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455; Elizabeth B. Weberg, Rolf T. Weberg and Richard R. Jones, Medical Products Division, E. I. du Pont de Nemours and Co., Brevard, North Carolina 28712

The scan-velocity dependence of friction force microscopy (FFM) is characterized on gelatin films and related to molecular relaxation in such glassy polymeric systems. For a subset of scanning parameters the velocity dependence of frictional force is affected by the measurement process, because of local heating in the tip-sample contact region: a peak in the friction-velocity relationship, attributed to the glass-to-rubber transition, shifts to higher velocity at increasingly perturbative scanning conditions. The ability to assess lateral inhomogeneities (of order 10 nm) in the frictional dissipation of energy is demonstrated. Frictional force images are transformed into "friction spectroscopy" data, i.e. histograms of frictional forces sensed over micron-scale regions. Narrow or broad histograms reflect the energy dispersion of relaxations triggered in glassy or rubbery regimes of behavior, respectively. These concepts are discussed in terms of low- or high-energy molecular conformations.

ABSTRACT. Please be BRIEF—150 words maximum if possible. Title of paper should be ALL CAPS; author(s) listed by first name, middle initial, last name; indicate address w/zip code. SINGLE SPACE, BLACK INK.

A. DIVISION OF Colloid and Surface Chemistry

B. MEMBER ☐ Yes ☒ No

C. TITLE OF PAPER
"Probing Molecular Relaxation on Polymer Surfaces with Friction Force Microscopy"

Please indicate preference: X oral _____ poster

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LUMINESCENCE AND MASS SPECTROMETRIC PROBES OF MECHANICAL DAMAGE IN CERAMICS.* J. Thomas Dickinson, Richard L. Webb, and Leslie C. Jensen, Washington State University, Pullman, WA 99164-2814

Abrasion and other tribological types of loading can produce significant dislocation motion on ceramic surfaces. The field of moving atoms in turn produces point defects in surprising abundance. We have developed methods to image the photoluminescence generated by these defects. In MgO, the resulting F-center aggregates yield a distinct 400-nm emission band. Unique patterns of these defects occur on cleavage surfaces where material is extensively deformed. Indentations, scratch marks, polishing grooves, and features induced by tribological interactions are readily observed and mapped. We discuss potential applications for detecting and quantifying damage at ceramic surfaces. We also report dynamic probes of damage involving mass spectrometric detection of mechanically-induced decomposition products during wear, which have implications concerning surface chemistry during tribological loading. *This work supported by DOE, AFOSR, and NSF.

Division of ~~Chemical Physics~~ Colloid and Surface Chemistry

Member: **Yes** No

Title of Paper: LUMINESCENCE AND MASS SPECTROMETRIC PROBES OF MECHANICAL DAMAGE IN CERAMICS.

Please indicate preference: **Oral** Poster

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ELECTRICAL CONDUCTIVITY MEASUREMENTS OF POLYMER THIN FILMS ON METAL SUBSTRATES.* **Kerry Hipps, J. Thomas Dickinson, and Leslie C. Jensen, Washington State University, Pullman, WA 99164-2814**

Topographical measurements by AFM and other nanometer scanning probes often do not adequately distinguish between phases along composite surfaces . In the case of insulator structures (e.g., thin films; particles) on metal substrates, nanometer scans of electrical conductivity offer a convenient tool for interpreting topography. Electrical contact is made with commercial Si_3N_4 AFM tips coated with Au, Ag, W, or Au-Pd. Voltages ranging from 100 mV to 10 volts are applied to the tip and the metal substrate is grounded through an electrometer to measure the resulting current. The tips are mounted in a commercial AFM (Digital Instruments Nanoscope III); topographical and current scans are acquired simultaneously in the contact mode. Freshly grown, 300-nm thick, polytetrafluoroethylene (PTFE) films on stainless steel substrates yield no measurable current. Thinner films or those exposed to mechanical abrasion exhibit numerous patches with two current levels—sub μA and > μA signals—which often correlate with topography. We interpret these signals and discuss possible applications to thin film characterization and tribology. ***This work supported by the National Science Foundation.**

Division of ~~Chemical Physics~~ Colloid and Surface Chemistry

Member: **Yes** No

Title of Paper: ELECTRICAL CONDUCTIVITY MEASUREMENTS OF POLYMER THIN FILMS ON METAL SUBSTRATES.

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FRICTION FORCE MICROSCOPY IN ULTRAHIGH VACUUM: AN ATOMIC SCALE STUDY

R. Lüthi, E. Meyer, H. Haefke, L. Howald and H.-J. Güntherodt, Institute of Physics, Condensed Matter Div., Experimental Physics, University of Basel, CH-4056 Basel,)
T. Gyalog and H. Thomas
(Condensed Matter Division, Theoretical Physics, ibid.)

We present an atomic-scale study on friction performed by a bidirectional scanning force microscope operated in ultrahigh vacuum. The measurements were performed on insulating surfaces of ionic crystals, such as NaF, NaCl, KBr, and AgBr. In order to guarantee well defined conditions, the samples were freshly prepared and studied in ultrahigh vacuum where contaminants can be excluded. The morphology and tribological properties of these clean surfaces are discussed. The method of the two-dimensional histogram technique is used to determine tribological properties quantitatively. By this technique, the normal force regimes of wearless friction and the initial stage of wear are extracted.

ABSTRACT. Please be BRIEF—150 words maximum if possible. Title of paper should be ALL CAPS; author(s) listed by first name, middle initial, last name; indicate address w/zip code. SINGLE SPACE, BLACK INK.

A. DIVISION OF Symposium on „Molecular Tribology"

B. MEMBER ☐ Yes ☒ No

C. TITLE OF PAPER Friction force microscopy in ultrahigh vacuum: an atomic scale study.

Please indicate preference: _____ oral ___X___ poster

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TWO-DIMENSIONAL STICK-SLIP MODEL COMBINED WITH EFFECTIVE ADHESIVE RADIUS

Seizo Morita, Satoru Fujisawa, Eigo Kishi and Yasuhiro Sugawara
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To explain the two dimensional nature of atomic scale friction with a lattice periodicity, we proposed a two-dimensional stick-slip model with a lattice periodicity. It accomplished quantitatively to interpret the observed behaviors of atomic scale friction such as, (1)wave forms, (2)averaged periodicities and (3)amplitudes of sawtooth and square-wave behaviors. However, there still remains several questions such as, (4)where the slip happens? and (5)which stick-point is the next stick-point?. Therefore, in order to explain the two dimensional nature of atomic scale friction with a lattice periodicity in more detail, we expanded the two-dimensional stick-slip model by taking account of an effective adhesive radius.

ABSTRACT. Please be BRIEF—150 words maximum if possible. Title of paper should be ALL CAPS; author(s) listed by first name, middle initial, last name; indicate address w/zip code. SINGLE SPACE, BLACK INK.

A. DIVISION OF Colloid and Surface Chemistry

B. MEMBER ☐ Yes ☑ No

C. TITLE OF PAPER

TWO-DIMENSIONAL STICK-SLIP MODEL
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EXAFS STUDIES OF THE STRUCTURE OF SPUTTER-DEPOSITED MoS_2 FILMS,

J. R. Lince, M. R. Hilton, and S. V. Didziulis, Surface Science Department, Mechanics and Materials Technology Center, The Aerospace Corporation, El Segundo, CA 90245, and A. S. Bommannavar, Brooklyn College of CUNY, Brooklyn, NY 11210.

Sputter-deposited MoS_2 films, including those cosputtered with various metals and sputtered metal/MoS_2 multilayers, are being used for the next generation of solid lubricated devices on spacecraft. Because of the films' poor crystallinities, relating film structure to tribological properties is difficult. The extended x-ray absorption fine structure (EXAFS) technique is ideal for studying these films because it is sensitive to short-range or local order. We obtained and analyzed EXAFS data for films produced by different sputtering methods, with varying oxygen and metal contents. The results were correlated with data obtained with XPS, EDX, and diffraction techniques. All films studied were shown to contain MoS_2 along with an $MoS_{2-x}O_x$ phase that exhibits an MoS_2-like structure, the latter phase predominating. Films with added metals contain MoS_2 and $MoS_{2-x}O_x$ that have not reacted with the cosputtered metals, but exhibit reduced crystallite sizes, resulting in beneficial densification of the films.

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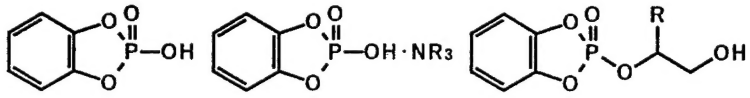
MOLECULAR DESIGN OF NOVEL LUBRICITY ADDITIVES: *ORTHO*–PHENYLENE PHOSPHATES.

Ichiro Minami, Department of Chemical Technology, Tokyo Institute of Technology, Tokyo, Japan.

Synthetic oils are found to have great advantages over mineral oils. Thus, new additive technology is much required to apply synthetic lubricants in practice. Conventional additives for mineral oils are usually ineffective for improving on synthetic oils. Since additive response depends on oil–additive correlation, additives that are suitable for individual synthetic oils have to be developed to achieve maximum performance. Phosphate–type novel lubricity additives were developed by taking molecular structure into account, as shown in this work. Diphenyl phosphate improved lubricity of neopentyl ester–type oils(ES) and polyether–type oils(PE) to some extent. However, it accelerates corrosion of iron. o–Phenylene phosphate(OPP), having a unique five–membered ring moiety, exhibit anti–wear and anti–seizure properties with less corrosivity. Optimized anti–wear agents were designed by chemical modification of OPP. Trialkylamine salts and hydroxyalkyl(alkenyl) esters were examined. They decelerate wear rate and prevent seizure without promote corrosion. Structure of R affects lubricity of OPP–TA in PE and OPP–HA in ES. Effects of R were considered as solubility in oil and adsorptivity on surface.



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A. DIVISION OF Molecular tribology

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C. TITLE OF PAPER Molecular Design of (Novel) Lubricity Additives: ortho-Phenylene Phosphates

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FLUORESCENCE PRECEDING AND ACCOMPANYING CARBON DEPOSITION IN SILICON NITRIDE FRICTION CONTACTS LUBRICATED BY ORGANIC VAPORS AT HIGH TEMPERATURES. J.L. Lauer, V. Prabhakaran, R. Kodama, and F.E. Talke, Center for Magnetic Recording Research, University of California, San Diego, La Jolla, California 92093-0401

Friction and wear in silicon nitride contacts above 350° can be reduced by as much as 95 and 99.9% respectively in the presence of a continuous stream of an inert gas containing a few percent of ethylene or other carbonaceous gas. Carbon formed on the contacting surfaces has been considered responsible for this result. To find the mechanism and the reason for the particular suitability of silicon nitride — e.g. zirconia was ineffective — experiments were conducted with a high-temperature pin-on-disk tribometer, and followed by fluorescence and Auger electron spectroscopies. Striking differences were found between the wear track and other surfaces, such as fluorescence intensities differering ten-times and up to 20% differences in Si/N atomic ratios. Thermally and mechanically induced surface defects are likely causes for the deposition and adsorption of the lubricating carbon and the associated phenomena.

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19. ABSTRACT

This contract provided funding for a Symposium entitled "Molecular Tribology" which was part of the American Chemical Society National Meeting held in Anaheim, California, April 4-6, 1995. Attendees, about 40 per session, came from many diverse disciplines - chemistry, physics, engineering, etc. - but all had a common interest in the molecular origins of tribology. Thirty four papers were presented on the following topics:

(i) atomic-scale simulations of tribology phenomena;

(ii) UHV surface science, atomic force microscopy, and surface force apparatus studies of the molecular origins of tribology;

(iii) tribological issues faced by the space, automotive, magnetic recording, and micro-mechanics industries.

Funding from the ONR grant was used to provide partial travel support for four of the twelve invited speakers. The program and abstracts are attached.